

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B01J 13/00		A1	(11) International Publication Number: WO 99/32218 (43) International Publication Date: 1 July 1999 (01.07.99)
<p>(21) International Application Number: PCT/EP98/08244</p> <p>(22) International Filing Date: 16 December 1998 (16.12.98)</p> <p>(30) Priority Data: 197 56 633.2 19 December 1997 (19.12.97) DE</p> <p>(71) Applicant (<i>for all designated States except US</i>): CABOT CORPORATION [US/US]; 75 State Street, Boston, MA 02109-1806 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (<i>for US only</i>): HARTEL, Johannes [DE/DE]; Hasselstrasse 39, D-65812 Bad Soden (DE). FORBERT, Rainald [DE/DE]; Harzweg 1, D-65439 Flörsheim (DE).</p> <p>(74) Agents: MAI, Peter et al.; John-F.-Kennedy-Strasse 4, D-65189 Wiesbaden (DE).</p>			<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p>

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: **A METHOD FOR THE SUB-CRITICAL DRYING OF LYOGELS TO PRODUCE AEROGELS**

(57) Abstract

The present invention refers to a method for the sub-critical drying of lyogels to produce aerogels. The method for the sub-critical drying of lyogels to produce aerogels provides for the lyogel particles to be disposed as a fixed bed and for a drying gas to be passed through them.

Description**A method for the sub-critical drying of lyogels to produce aerogels**

The invention relates to a method for the sub-critical drying of lyogels to produce aerogels.

Lyogels are gels which contain a liquid, the dispersing agent. In the particular instance where the gel fluid is water, they are also referred to as hydrogels. In the present Application, the term 'lyogel' also includes hydrogels. Aerogels in the wider sense, i.e. in the sense of "gel with air as the dispersant", a suitable gel is produced by drying. The term "aerogels" in this sense includes aerogels in the narrower sense, xerogels and cryogels. In this respect, a dried gel is referred to as an aerogel in the narrower sense if the fluid of the gel is eliminated at temperatures above the critical temperature and starting from pressures which are above the critical pressure. On the other hand, if the fluid of the gel is removed sub-critically, for example with the formation of a fluid-vapour interface, then the resulting gel is also frequently referred to as a xerogel.

Where the use of the term aerogels in the present Application is concerned, there are gels which are sub-critically dried.

Aerogels have a very low density and high porosity for solid substances. Therefore, and on account of the minimal pore size, aerogels, particularly those with porosities of over 60% and densities below 0.6 g/cu.cm, display an extremely low thermal conductivity and are therefore used as heat insulating materials such as are described for instance in EP-A 0 171 722.

For industrial applications, aerogels are predominantly used as granulate. For the application, it is in this respect essential for the aerogel granulate to be used to consist of particles of a suitable form, preferably spherical form, and size distribution.

By virtue of their low density, however, aerogels also exhibit low mechanical stability, particularly in respect of sheer loadings and against abrasion.

By reason of the capillary forces which occur in sub-critical drying and the shrinkage involved, not all lyogels are suitable for sub-critical drying to produce an aerogel. During drying, the gel shrinks considerably if the meniscus of the fluid migrates into the interior of the gel, in order, with effect from a certain point in the drying process, to spring back more or less completely into its starting form again. Consequently, depending upon the qualities of the inner gel surface, a certain minimum stability of the gel network is essential, modification of the inner gel surface often being required in order to prevent a reaction by adjacent pore walls in the shrunk condition and a collapse of the gel which this would entail.

Corresponding processes in which the inner surface of an SiO_2 lyogel is organically modified and the resulting gel is sub-critically dried to produce an aerogel, are disclosed for example in US-A-5 565 142, DE-A-43 42 548 and in the unpublished German Patent Application 19648798.

Gels which are unsuitable for sub-critical drying collapse under sub-critical drying, with a loss of the porous structure and therefore they no longer display the favourable properties of aerogels.

According to the gel, surface modification, granular form and size and drying conditions, so gel particles can, during drying, be destroyed on a macroscopic scale, i.e. while retaining the nanoporous structure. It is true that the aerogel retains its properties but on account of the now smaller granular size an irregular or undefined grain shape, it can no longer be used so satisfactorily.

Drying methods which at first sight appear obvious for such drying problems are not readily suited to major industrial production of aerogel granulate of a definite form.

By reason of the low density of the aerogels, a fluid bed drying system has been found to be unsuited to major industrial production. In order not to carry the aerogel particles out of the layer, it would be necessary to work below the fluidising point; the necessary gas flow velocities would then be so low that there would be no guarantee of heat being supplied and vapour dispersed in an acceptable time for drying. Were greater gas flow velocities to be used, then the aerogel would not be completely dried since it will be conveyed out of the dryer. Furthermore, in the fluidised phase, gel particles collide with one another so that there is considerable abrasion and grain fracture.

Contact drying proves to be not sufficiently effective since due to the high heat insulating capacity of the aerogels, a transfer of heat into layers more remote from the contact surface does not take place quickly enough so that only minimal layer thicknesses and therefore, in view of the quantities needed, excessively great surface areas would be needed.

In accordance with DE-A-43 16 540, aerogels are dried by dielectric processes. Due to the necessary electrical energy and the relatively high investment for an appropriate drying apparatus, however, these methods are not sufficiently economical.

Therefore, the object of the present invention was to provide a method for the sub-critical drying of lyogels which are suitable for sub-critical drying to produce aerogels and which minimises the destruction of aerogel particles and the abrasion of aerogel particles during drying and which can be used on a large industrial scale.

Surprisingly, the problem is resolved by a method for the sub-critical drying of lyogels to produce aerogels and which is characterised in that the lyogel particles are disposed as a static bed and have a dry gas flowing through them.

Carried out in this way, the drying does not lead to grain fracture or abrasion since the particles are stationary in their bulk. Surprisingly, the drying can be carried out in relatively short times and in layer heights which are considerable for fixed bed drying.

In principle, any lyogels which can be dried sub-critically are suitable for the method, i.e. their gel structure must be sufficiently stable to withstand collapse of the framework by the action of capillary forces and are if necessary suitably surface modified in order for example to prevent a reaction between pore walls in the shrunken condition.

Where the lyogels are concerned, these may according to the type of gel structure be organic or inorganic lyogels. For example, they can be produced on a basis of metal oxides which are suitable for the Sol-gel technical (G. J. Brinker, G. W. Scherer, Sol-Gel Science 1990, chapters 2 and 3), such as for example Si- or Al-compounds or on the basis of organic substances which are suitable for the sol-gel technique such as for example melamine formaldehyde condensates (US-A-5 086 085) or resorcin formaldehyde condensates (US-A-4 873 218) or even on the basis of mixtures of the above-mentioned materials. Preferably, they are SiO₂ gels and particularly preferably organically surface modified SiO₂ gels such as are described for example in the unpublished German Patent Application No. 19648798.

Where the gel fluid is concerned, this may in principle be pure substances or mixtures, the gel fluid preferably containing more than 50% by weight of organic solvents, preferably acetone or hexamethyl disiloxane. Naturally, the gel fluid may also contain small quantities of other substances such as for example hydrochloric acid or residues of water.

The lyogel particles can in principle be of any desired form and size but preferably substantially spherical particles with diameters between 100 µm and 5 cm and particularly preferred are those with diameters between 0.5 mm and 5 mm. It is also possible to dry mixtures of particles of different shape and/or different size.

In order to avoid already dried and therefore lightweight aerogel particles being blown away, it would among other things be necessary for the velocity of the dry gas flow to be low so that no dried aerogel particles are carried away. However, this results in low gas flows and therefore a very limited energy input. For drying aerogels, a rapid energy input is advantageous. For using relatively high drying gas flow velocities, the bulk must therefore, at those places where the gas flow emerges from the fixed bed, be limited by at least one arrangement which is permeable to the drying gas but not to the particles.

Surprisingly, the fixed bed is preferably and in per se known manner, traversed by the drying gas flow passing through it downwards, so that the arrangement which is permeable to the drying gas but not to the particles is constituted by the carrier of the fixed bed. The drying apparatus which is then to be used is consequently not only simpler and less expensive but grain fracture is also reduced, since the upper layers which press down onto those underneath are the first to be dried. The dried and mechanically sensitive aerogels then lie on the heavier and less dried and also mechanically loadable gel particles and are not heavily loaded mechanically.

For a continuous operation, the fixed bed may also be moved with the carrier, e.g. on a suitable belt. Preferably, the gas flow then passes through the fixed bed crosswise to the direction of movement.

The thickness of the fixed bed in the direction of flow of the drying gas stream can be surprisingly great. Preferably, it is between 20 cm and 100 cm and particularly preferably between 20 and 60 cm.

Any gas suitable for drying can be used as the drying gas; if the gel fluid contains large fractions of organic solvents, then possibly an inert gas such as nitrogen should be used. The input gas flow can already contain solvent gas which the process allows, in other words a circulatory pattern of gas flow, whereby, as usual, solvent gas is constantly

eliminated from the circuit, for example by condensation. To accelerate the drying as a whole, it may be advantageous first to dry the gel in a circulatory fashion but to use fresh drying gas for drying the last residues of gel fluid.

The method according to the invention can be carried out by apparatus known to the man skilled in the art, e.g. fixed bed driers, suitable containers with screen bottoms or suitable drying belts, etc., which may possibly be modified in a manner evident to a man of the art.

Preferably, the method for drying surface modified SiO_2 aerogels such as disclosed for example in DE-A-43 42 548 or in the unpublished German Patent Application 196 487 98 will be used.

In this case, if the gel fluid contains more than 50% by weight hexamethyl disiloxane or acetone, then the temperature of the drying gas is preferably between 100°C and 200°C and with particular preference between 140°C and 180°C.

In the case of the said surface modified SiO_2 aerogels, the incident flow velocities are preferably in the range between 1 and 40 cm/s and particularly preferably between 5 and 30 cm/s.

Although the method is particularly suitable for producing aerogels with densities below 300 g/cu.cm, it is also possible to use it for drying xerogels of greater density.

The method according to the invention will be described hereinafter with reference to an example of embodiment but without however being limited thereby.

Example:

A surface modified SiO_2 lyogel which has been produced in accordance with examples 1 to 4 in the unpublished German Patent Application 1964877798 and which has a sharp

grain size distribution around 1 mm diameter is dried in a fixed bed with a height of 50 cm with a stream of nitrogen flowing through the fixed bed from the top downwards at an incident flow velocity of 20 cm/s and with a gas inlet temperature of 160°C. Initially, the gel is dried for 2½ hours in a circulatory manner, the drying gas leaving the fixed bed saturated with moisture and after thorough condensation with a charge of 10g/kg inert gas, it is again introduced into the fixed bed. Afterwards, drying is continued for half-an-hour with fresh drying gas. The dried aerogel displays virtually no grain fracture and hardly any abrasion.

Patent claims

1. A method for the sub-critical drying of lyogels to produce aerogels, characterised in that the lyogel particles are disposed as a fixed bed and have drying gas passed through them.
2. A method according to claim 1, characterised in that, at those locations at which the gas flow emerges from the fixed bed, the fixed bed is bounded by at least one arrangement which is permeable to the drying gas but not to the particles.
3. A method according to claim 2, characterised in that the fixed bed lies on the said means and has the flow passing through it from the top downwards.
4. A method according to at least one of claims 1 to 3, characterised in that the lyogel is an organically modified gel the framework of which contains SiO_2 .
5. A method according to claim 4, characterised in that the gel fluid predominantly contains hexamethyl disiloxane.
6. A method according to claim 4, characterised in that the gel fluid predominantly contains acetone.
7. A method according to at least one of claims 4 to 6, characterised in that the temperature of the drying gas at the inlet is between 100°C and 200°C.
8. A method according to 6 or 7, characterised in that the incident flow velocity is between 1 cm/s and 40 cm/s.

9. A method according to at least one of the preceding claims, characterised in that the thickness of the fixed bed is between 20 cm and 100 cm in the direction of flow of the drying gas stream.
10. A method according to at least one of the preceding claims, characterised in that the drying gas follows a circulatory system.
11. A method according to at least one of the preceding claims, characterised in that in a first phase of drying the drying gas is circulated while in a second phase fresh drying gas is used.
12. A method according to at least one of the preceding claims, characterised in that the fixed bed is moved together with the means bounding it, the stream of drying gas being passed through the fixed bed crosswise to the direction of movement.

PCT

WELTORGANISATION FÜR GEISTIGES EIGENTUM
Internationales Büro



INTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE
INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

(51) Internationale Patentklassifikation ⁶ : B01J 13/00		A1	(11) Internationale Veröffentlichungsnummer: WO 98/50144 (43) Internationales Veröffentlichungsdatum: 12. November 1998 (12.11.98)
(21) Internationales Aktenzeichen: PCT/EP98/02519		(81) Bestimmungsstaaten: CA, CN, JP, KR, MX, NO, US, europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) Internationales Anmeldedatum: 29. April 1998 (29.04.98)		Veröffentlicht <i>Mit internationalem Recherchenbericht. Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist; Veröffentlichung wird wiederholt falls Änderungen eintreffen.</i>	
(30) Prioritätsdaten: 197 18 740.4 2. Mai 1997 (02.05.97)		DE	
(71) Anmelder (für alle Bestimmungsstaaten ausser US): CABOT CORPORATION [US/US]; 75 State Street, Boston, MA 02109 (US).			
(72) Erfinder; und (75) Erfinder/Anmelder (nur für US): SCHMIDT, Marc [DE/DE]; Rauenthaler Weg 33, D-60529 Frankfurt am Main (DE).			
(74) Anwälte: MAI, Peter usw.; Luderschmidt, Schüler & Partner, John-F. Kennedy Strasse 4, Postfach 3929, D-65029 Wiesbaden (DE).			

(54) Title: METHOD FOR GRANULATING AEROGELS

(54) Bezeichnung: VERFAHREN ZUR GRANULIERUNG VON AEROGELEN

(57) Abstract

The invention relates to a method for agglomerating aerogel particles. According to said method, the aerogel particles are placed in a mixing device and mixed thoroughly, a binding agent also being added to said mixing device.

(57) Zusammenfassung

Die vorliegende Erfindung betrifft ein Verfahren zur Aufbauagglomeration von Aerogel-Partikeln, bei dem die Aerogel-Partikel in eine Mischvorrichtung gegeben und durchmischt werden, und der Mischvorrichtung ein Bindemittel zugeführt wird.

Beschreibung

Verfahren zur Granulierung von Aerogelen

Gegenstand der vorliegenden Erfindung ist ein Verfahren zur Granulierung von Aerogelen.

Aerogele, insbesondere solche mit Porositäten über 60 % und Dichten unter 0,6 g/cm³, weisen eine äußerst geringe thermische Leitfähigkeit auf und finden deshalb Anwendung als Wärmeisolationsmaterial, wie in der EP-A-0 171 722 beschrieben, als Katalysatoren oder Katalysatorträger, sowie als Adsorptionsmaterial. Darüber hinaus ist die Verwendung für Čerenkov-Detektoren aufgrund ihrer für Feststoffe sehr geringen Brechzahl bekannt. Weiterhin ist in der Literatur aufgrund ihrer besonderen akustischen Impedanz eine mögliche Verwendung als Impedanzanpassung z.B. im Ultraschallbereich beschrieben.

Auch ist ihre Anwendung als Träger für Wirkstoffe in Pharmazie oder Landwirtschaft möglich.

Aerogele im weiteren Sinn, d.h. im Sinne von "Gel mit Luft als Dispersionsmedium", werden durch Trocknung eines geeigneten Gels hergestellt. Unter den Begriff "Aerogel" in diesem Sinne, fallen Aerogele im engeren Sinn, Xerogele und Kryogele. Dabei wird ein getrocknetes Gel als Aerogel im engeren Sinn bezeichnet, wenn die Flüssigkeit des Gels bei Temperaturen oberhalb der kritischen Temperatur und ausgehend von Drücken oberhalb des kritischen Druckes weitestgehend entfernt wird. Wird die Flüssigkeit des Gels dagegen unterkritisches, beispielsweise unter Bildung einer Flüssig-Dampf-Grenzphase

getrocknet werden kann. Auf dieser Trocknungstechnik basierende Herstellungsverfahren sind z.B. aus der EP-A-0 396 076 , der WO 92/03378 oder der WO 95/06617 bekannt.

Die mit der überkritischen Trocknung von Aerogelen verbundene Hochdrucktechnik ist jedoch verfahrenstechnisch aufwendig und birgt ein hohes Sicherheitsrisiko. Zudem ist die überkritische Trocknung von Aerogelen ein sehr kostenintensives Herstellungsverfahren.

Eine Alternative zur überkritischen Trocknung bietet ein Verfahren zur unterkritischen Trocknung von SiO_2 -Gelen.

Die mit der unterkritischen Trocknung verbundenen Kosten sind aufgrund der einfacheren Technik, den niedrigeren Energiekosten und dem geringeren Sicherheitsrisiko wesentlich geringer.

Das SiO_2 -Gel kann dabei beispielsweise durch saure Hydrolyse von Tetraalkoxysilanen in einem geeigneten organischen Lösungsmittel mittels Wasser erhalten werden. Nach Austausch des Lösungsmittels gegen ein geeignetes organisches Lösungsmittel wird in einem weiteren Schritt das erhaltene Gel mit einem Silylierungsmittel umgesetzt. Das dabei entstehende SiO_2 -Gel kann anschließend aus einem organischen Lösungsmittel heraus an der Luft getrocknet werden. Damit können Aerogele mit Dichten unter $0,4 \text{ g/cm}^3$ und Porositäten über 60 % erreicht werden. Das auf dieser Trocknungstechnik basierende Herstellungsverfahren ist ausführlich in der WO 94/25149 beschrieben.

Die oben beschriebenen Gele können darüber hinaus vor der Trocknung in der alkohol-wäßrigen Lösung mit Tetraalkoxysilanen versetzt und gealtert werden, um die Gelnetzwerkstärke zu erhöhen, wie in der WO 92/20623 offenbart.

eine Wirbelschichtapparatur, werden die Aerogel-Partikel in Bewegung gebracht, so daß sie eine Relativbewegung untereinander haben.

Vorteilhafterweise wird das Bindemittel als wässrige oder nichtwässrige Lösung oder Suspension oder auch als Schmelze, z.B. durch Verdüsen, eingebracht. Das Bindemittel führt zu einer Zusammenballung der primär vorgelegten Aerogel-Partikel zu größeren Agglomeraten.

Das Bindemittel führt dabei durch chemische Reaktion, Erstarren, Auskristallisieren infolge Verdunstung oder Verdampfung des Lösungsmittels, gegebenenfalls auch unter Einwirkung erhöhter Temperaturen, zu einer Verbindung der Mischungsbestandteile.

Gemäß einer weiteren vorteilhaften Ausführungsform wird das Bindemittel als Feststoff zugegeben. Die Bindung erfolgt dann durch chemische Reaktion des Feststoffes mit einer oder mehrerer Komponenten der Mischung, oder durch die Erweichung eines festen Bindemittels, z.B. durch erhöhte Temperaturen, wodurch es klebrig wird und die Partikel der Mischung verbindet.

Eine andere zweckmäßige Ausführungsform sieht vor, daß zusätzlich zu den Aerogel-Partikeln noch Additive und/oder Füllstoffe, die partikel- oder faserförmig vorliegen können, in die Mischvorrichtung gegeben werden.

Eine bevorzugt Ausführungsform sieht vor, daß die Agglomerate ihrer Größe nach separiert werden. Dies geschieht vorteilhafterweise, indem aus den entstandenen Granulaten die Zielfraktion entsprechend dem gewünschten Korngrößenbereich abgesiebt wird. Granulate, die zu groß sind können gegebenenfalls zerkleinert, beispielsweise mit einem Zerhacker oder Messerkopf, und gesiebt werden, so daß sie im gewünschten Korngrößenbereich liegen oder nach der Zerkleinerung dem Agglomerierapparat wieder zugeführt werden. Granulate, die zu klein sind können gegebenenfalls dem Agglomerierapparat wie-

der zugeführt werden.

Gemäß einer weiteren Ausführungsform werden die Agglomerate vor einer weiteren Verarbeitung getrocknet.

8. Verfahren gemäß Anspruch 7, dadurch gekennzeichnet, daß die zerkleinerten und unter dem gewünschten Korngrößenbereich liegenden Agglomerate der Mischvorrichtung zugeführt werden.
9. Verfahren gemäß mindestens einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Agglomerate vor einer weiteren Verarbeitung getrocknet werden.